2 FR 1392152

PATENT SPECIFICATION

1,020,304

NO DRAWINGS

1,020,304

Date of Application and filing Complete Specification: April 8, 1964.
No. 14475/64.
Application made in Germany (No. F39467 IVc/22e) on April 11, 1963.
Complete Specification Published: Feb. 16, 1966.

Index at acceptance:—C4 PD1T
Int. Cl.:—C 09 b

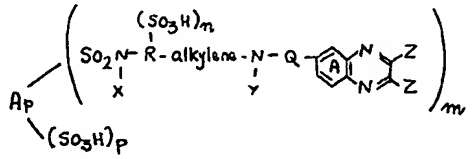
COMPLETE SPECIFICATION

Phthalocyanine Dyestuffs

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new phthalocyanine dyestuffs and with the preparation thereof.

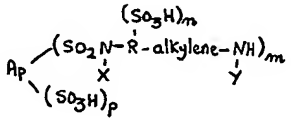
The new phthalocyanine dyestuffs according to the present invention can, in the free acid state, be represented by the general formula:—



(I)

wherein Ap means the radical of a metal-containing phthalocyanine dyestuff, R is an aromatic carbocyclic radical, preferably a phenylene radical, X and Y, which may be the same or different, denote hydrogen atoms or unsubstituted or substituted alkyl, aralkyl or cycloalkyl radicals, "alkylene" denotes an alkylene radical containing 1—4 carbon atoms, one Z means a halogen atom, preferably a chlorine or bromine atom, and the other Z means a halogen atom, preferably a chlorine or bromine atom, or the residue of a hydroxy compound linked to the heterocyclic ring *via* the —O— atom, Q stands for —OC— or —O_2S—, n is 0, 1 or 2, m an integer of from 1—4 and p is an integer of from 1—8, the sum of p and m being less than 9; and wherein the ring A may contain further substituents.

The new dyestuffs of general formula (I) are prepared in the usual manner by condensation of appropriate starting components. The most advantageous process takes place in that, in dyestuffs of the general formula:—

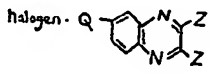


(II)

wherein Ap, R, X, Y, "alkylene", m, n and p have the meanings indicated above, the terminal group —NH is condensed with a compound of the general formula:—

[*Price 4s. 6d.*]

Price 33p



(III)

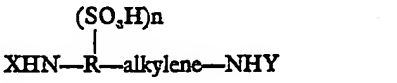
wherein Q and Z have the above significance and "halogen" stands for a halogen atom, preferably a chlorine or bromine atom.

As reactive components there may be used, for example, 2,3-dihaloquinoxaline carboxylic acid halides or sulphonic acid halides, such as 2,3-dichloroquinoxaline-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-8-methyl-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-5-chloro-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-7-chloro-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-8-chloro-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-5,8-dichloro-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-7-nitro-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-8-methylsulphonyl-6-carboxylic acid chloride, 2,3-dichloroquinoxaline-7-methoxy-6-carboxylic acid chloride, 2-chloro-3-methoxyquinoxaline-6-carboxylic acid chloride and the corresponding sulphonic acid chlorides.

If, in the dyestuffs obtained, both radicals Z represent halogen atoms, one of them may be replaced by the residue of a hydroxy compound linked to the heterocyclic radical by the —O— atom, which, in turn, may contain a reactive group, for example, an esterified hydroxy-alkyl group. In principle, the presence in the dyestuff of two or more reactive groups which are different from each other is possible. In any case, the final dyestuff should contain at least one and not more than four reactive groups of the general formula:—

(IV)

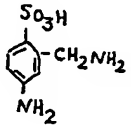
The compounds of general formula (II) required for the synthesis of the reactive dyestuffs of general formula (I) are synthesised by known methods in such a manner, for example, that a metal-containing phthalocyanine acid halide, such as a copper or nickel phthalocyanine tri- or tetrasulphonic acid chloride, is condensed, preferably in an aqueous acid medium, with an amino compound of the general formula:—



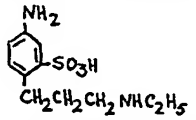
(V)

wherein X, Y, R, "alkylene" and n have the meanings indicated above and which contains the amino group directly linked to the radical R, to give the corresponding sulphonic acid amide derivative, and any unreacted excess acid halide groups in the radical of the phthalocyanine dyestuff are saponified to sulphonic acid groups. When carrying out this reaction, it is, in some cases, expedient to protect the amino group not intended for the reaction, at the alkylene radical of the compound of general formula (V), for example, by acylation. If, for this purpose, a reactive acylation component (III) is used, this represents already a mode of carrying out the modified process for the production of the new dyestuffs. When non-reactive acylation agents, for example, acetyl chloride, are used, the protected acylamino group is saponified after the completed reaction of the phthalocyanine acid halides with the monoacylamino components, in order to react it subsequently with an acylating agent (III).

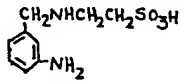
Examples of amino compounds of general formula (V) include 3-amino-benzylamine-6-sulphonic acid.



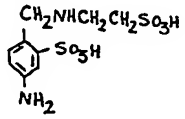
4-[1¹-N-ethylamino-propyl-(3¹)]-1-aminobenzene-3-sulphonic acid



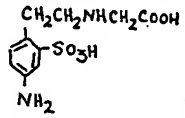
4-amino-benzylamine-2-sulphonic acid, N-(3-aminobenzyl)-taurine



N-(4-amino-2-sulphobenzyl)-taurine



and N-β (4-aminophenyl-2-sulpho)-ethyl-glycine



Metal-containing phthalocyanine dyestuffs from which the new dyestuffs can be prepared include, for example, copper and nickel phthalocyanine di- or tetrasulphonic acids and their halides, copper and nickel tetraphenylphthalocyanines with 2—8 sulphonic acid halide groups as well as sulphonic acid halides of chlorinated copper phthalocyanines.

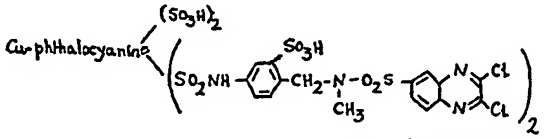
The new dyestuffs are valuable products which, as so-called fibre-reactive dyestuffs, are excellently suited for the dyeing and printing of cellulose-containing fibre materials, such as native or regenerated cellulose and of amide group-containing materials, such as wool and synthetic polyamide fibres. Depending upon the degree of their solubility, the dyestuffs are used in the form of aqueous solutions or suspensions. Excellent results are achieved when hydroxyl group-containing fibre materials, such as native and regenerated cellulose, are dyed or printed with the new dyestuffs according to the methods known for the use of reactive dyestuffs. They are generally used in the presence of acid-binding agents, such as alkalis, alkali metal carbonates and alkali metal bicarbonates, with or without simultaneous or subsequent heat-treatment.

The following Examples are given for the purpose of illustrating the present invention:—

EXAMPLE 1:

A neutral paste of copper phthalocyanine-3,3¹,3¹¹,3¹¹¹-tetrasulphonic acid chloride, prepared from 300 g. technical 96% copper phthalocyanine, is mixed with a little water and made up to 2 litres. 216 g. N-methyl-N-(4-amino-2-sulphobenzyl)-amine are introduced and dissolved by the addition of 80 ml. (95 g.) 37% hydrochloric acid. 150 ml. (148 g.) pyridine are then added dropwise at 0—3° C. in the course of 2 hours and the temperature slowly raised to 20° C. The temperature then spontaneously rises, while the acid is buffered, in the course of 1—1.5 hours, by the dropwise addition of a dilute sodium hydroxide solution. At 25—30° C. and a pH of 6.0, the resultant copper phthalocyanine tetra sulphonic acid-di-(3¹-sulpho-4¹-methylamino-methyl-anilide) is obtained in a dissolved state. The pyridine is subsequently distilled off by steam at a pH of 9.

300 g. 2,3-dichloroquinoxaline-6-sulphonic acid chloride are sprinkled into the reaction mixture, while stirring, and the pH is maintained, by the dropwise addition of dilute sodium hydroxide solution, at 8—9 until it remains unchanged. The dyestuff is kept in solution by the addition of water. 10 litres of dyestuff solution are finally obtained. After removing the solid, technical impurities, the pH is adjusted to 7.0 and the resultant dyestuff, which corresponds in its free acid form to the formula:—



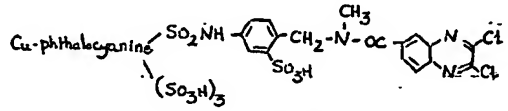
is precipitated by stirring in 1200 g. solid sodium chloride and isolated by suction filtration and drying.

If, instead of copper phthalocyanine-3,3¹,3¹¹,3¹¹¹-tetrasulphonic acid chloride, the equivalent amount of nickel phthalocyanine-3,3¹,3¹¹,3¹¹¹-tetrasulphonic acid chloride is used as starting component, a dyestuff is obtained which also exhibits excellent fastness properties and a similar shade.

EXAMPLE 2:

A suspension of 0.5 mol copper phthalocyanine-3,3¹,3¹¹,3¹¹¹-tetrasulphonic acid chloride, prepared as described in Example 1, is treated with 108 g. N-methyl-N-(4¹-amino-2¹-sulphobenzyl)-amine and 40 ml. concentrated hydrochloric acid, the reaction being initiated by the dropwise addition of 150 ml. (148 g.) pyridine at 0—3° C. and completed at 20—30° C. For buffering the acid to pH 6, 1120 ml. 10% sodium hydroxide solution are used. A solution of copper phthalocyanine tetrasulphonic acid-mono-(3¹-sulpho-4¹-methylaminomethyl-anilide) is obtained, from which the pyridine is removed by steam at pH 9.

For the reaction with 2,3-dichloroquinoxaline-6-carboxylic acid chloride, the product is cooled to 25° C. and the solution made up to 5 litres. 140 g. 2,3-dichloroquinoxaline-6-carboxylic acid chloride are then sprinkled in and the pH adjusted, whilst stirring, to 8—9 by the dropwise addition of a sodium hydroxide solution until, after about 7 hours, it remains unchanged. The dyestuff solution is freed from impurities by filtration and, after the mixture has been neutralised, the dyestuff, which in its free acid state corresponds to the formula.



is precipitated by stirring in sodium chloride, then filtered off with suction and dried.

The dyestuff is distinguished by a particularly good water-solubility.

If, using instead of copper phthalocyanine-3,3¹,3¹¹,3¹¹¹-tetrasulphonic acid chloride, the equivalent quantity of nickel phthalocyanine-3,3¹,3¹¹,3¹¹¹-tetrasulphonic acid chloride or of copper phthalocyanine-4,4¹,4¹¹,4¹¹¹-tetrasulphonic acid chloride or of copper phthalocyanine-3,4,4¹,4¹¹-tetrasulphonic acid chloride, the reaction takes an analogous course and the dyestuffs thus obtained show the same good water-solubility.

EXAMPLE 3:

A neutral paste of copper phthalocyanine-3,3¹,3¹¹-trisulphonic acid chloride, prepared from 600 g. technical 96% copper phthalocyanine, is stirred with a little water, made up to 4 litres and reacted at pH of 3.5—6.0 with 216 g. N-methyl-N-(4¹-amino-2¹-sulphobenzyl)-amine, initially at 0—3° C. and finally at 20—35° C., with the addition of 300 ml. (295 g.) pyridine and the pyridine then distilled off with steam at pH 9.0 from the resultant solution of copper phthalocyanine-trisulphonic acid-mono-(3¹-sulpho-4¹-methylaminomethyl anilide). The solution is cooled to 30° C., and 340 g. finely-powdered 2,3-dichloroquinoxaline-6-carboxylic acid chloride are sprinkled in portionwise, in the course of 4—6 hours, and a pH of 7.5 to 9.5 is maintained by the addition of a dilute sodium hydroxide solution. At the same time, the reaction mixture is diluted with sufficient water to keep the dyestuff in a dissolved state.

10 litres of a dyestuff solution are obtained which is separated from an excess of the acylating agent, adjusted to pH 7.0 by the addition of acetic acid and precipitated by stirring in 2.4 litres of a concentrated sodium chloride solution.

After suction filtration and drying at 50° C., a clear turquoise-blue dyestuff is obtained which is fixed on cotton from an alkaline, sodium carbonate-containing solution at 70—90° C., with a very good yield and fastness to light, washing, water,

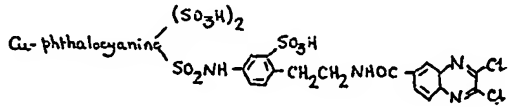
perspiration, alkalis (spotting), dry cleaning, mercerizing, rubbing and ironing; the dyeings are also crease-resistant.

The aliphatic amino group which remained free in the primary reaction product can be reacted in the same manner and with the same good result with 2,3-dichloroquinoxaline-6-sulphonic acid chloride instead of with dichloroquinoxaline carboxylic acid chloride.

When using nickel phthalocyanine-3,3¹,3¹¹-trisulphonic acid chloride as starting material, a slightly more greenish-turquoise blue is obtained which shows equally good properties.

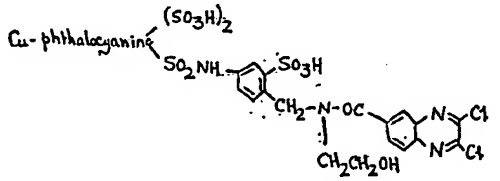
EXAMPLE 4:

A neutral paste of copper phthalocyanine-trisulphonic acid chloride, prepared from 50 g. 96% copper phthalocyanine, is stirred with water and made up to 350 ml. and 18 g. 1-(β-aminoethyl)-4-aminobenzene-2-sulphonic acid are introduced and dissolved by the addition of 7 ml. concentrated hydrochloric acid. The reaction is initiated by the dropwise addition of 25 ml. pyridine at 0—3° C. and at a pH of 2.5 and completed in the course of 4—6 hours by raising the temperature to 30° C. and the pH to 6.0 by the dropwise addition of 10% sodium carbonate solution. A solution of copper phthalocyanine-trisulphonic acid-mono-(3¹-sulpho-4¹-β-aminoethyl)-anilide is obtained, from which the pyridine is distilled off by steam at pH 9. The solution is cooled to 30° C. and, at pH 8.5—9, reacted with 24 g. 2,3-dichloroquinoxaline-6-carboxylic acid chloride. The pH is maintained by the dropwise addition of dilute sodium carbonate solution. The reaction is completed after about 8 hours. The reaction mixture is filtered, the filtered dyestuff solution rendered acidic with acetic acid and the dyestuff precipitated therefrom by stirring the solution into 1400 ml. of a concentrated solution of sodium chloride. The dyestuff thus obtained corresponds, in its free acid state, to the formula:



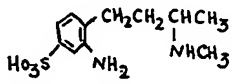
EXAMPLE 5:

A paste of copper phthalocyanine-3,3¹,3¹¹-trisulphonic acid chloride, prepared from 40 g. 96% copper phthalocyanine, is reacted, in an analogous manner to the method given in Example 3, first with 16.4 g. N-β-hydroxyethyl-N-(4¹-amino-2¹-sulphobenzyl)amine and subsequently with 2,3-dichloroquinoxaline-6-carboxylic acid chloride. A dyestuff is obtained which shows properties equally as good as the dyestuff of Example 3. The dyestuff obtained corresponds, in its free acid state, to the formula:—

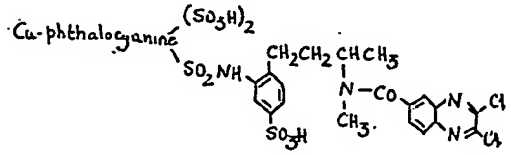


EXAMPLE 6:

By proceeding according to the description given in Example 5 and using, instead of N-β-hydroxyethyl-N-(4¹-amino-2¹-sulphobenzyl)-amine, the equivalent amount of γ-methylamino-α-(amino-sulphophenyl)-butane of the probable formula:—

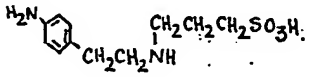


a dyestuff is obtained which dyes cotton clear blue shades; it corresponds, in its free acid state, to the probable formula:—



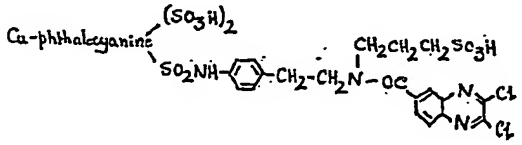
EXAMPLE 7:

A neutral aqueous paste of cobalt phthalocyanine-trisulphonic acid chloride, prepared from 25 g. cobalt phthalocyanine, is stirred with water and made up to 175 ml. 11 g. aminophenylethylamino-γ-propane sulphonic acid of the probable formula:—



are added thereto, the condensation is initiated at 0° C. by slowly adding 13 ml. pyridine, whilst stirring, and completed at room temperature. The cobalt phthalocyanine trisulphonic mono-anilide derivative is dissolved at pH 6 by the dropwise addition of sodium carbonate solution, and the pyridine distilled off at pH 9.

The product obtained is reacted in an aqueous solution with 14 g. 2,3-dichloroquinoxaline-6-carboxylic acid chloride in such a manner that the finely-powdered acid chloride is sprinkled into the reaction solution and a pH of 8.5—9.0 is maintained at 30° C., for 6 hours, by the dropwise addition of dilute sodium carbonate solution. Finally, the dyestuff solution is filtered and the pH adjusted to 7.0; the dyestuff is precipitated by the addition of sodium chloride, filtered off with suction and dried at 50° C., in a vacuum. A reactive dyestuff is obtained which, in its free acid state, corresponds to the probable formula:—

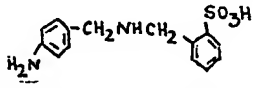


and which dyes cotton in dull blue shades.

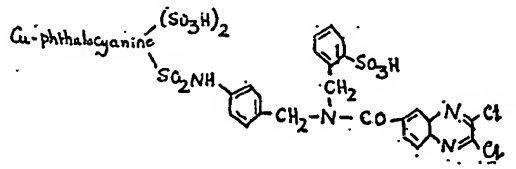
If, instead of 11 g. amino-phenylethylamino-γ-propane sulphonic acid, 11.75 g. amino-phenylethylamino-δ-butane sulphonic acid are used for carrying out the reaction, a dyestuff with similar properties is obtained.

EXAMPLE 8:

A neutral, aqueous paste of cobalt phthalocyanine trisulphonic acid chloride, prepared from 25 g. cobalt phthalocyanine, is stirred with water and made up to 175 ml. 12.5 g. N-(2¹-sulphobenzyl)-N-(aminobenzyl)-amine of the probable formula:—

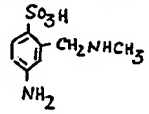


and 12.5 ml. pyridine are introduced. The mixture is stirred for some hours, whilst cooling with ice, the temperature then raised, in the course of several hours, and the pH raised by the dropwise addition of dilute sodium carbonate solution until, at pH 6 and a temperature of 40° C., the starting components are dissolved. The pyridine is then distilled off by steam, the solution made up to 500 ml. and the dyestuff subsequently acylated with 2,3-dichloro-quinoxaline-6-carboxylic acid chloride at 30° C. and at a pH of 8.5—9.0. After removing the impurities, the dyestuff solution is precipitated at pH 7 with 100 g. sodium chloride and the dyestuff isolated by filtering with suction and dried at 50° C. in a vacuum. The dyestuff thus obtained corresponds, in its free acid state, to the probable formula:—



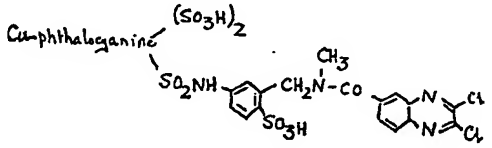
EXAMPLE 9:

An aqueous paste of cobalt phthalocyanine-trisulphonic acid chloride, prepared from 25 g. cobalt phthalocyanine, is stirred with water and made up to 175 ml. 9 g. N-(5-amino-2-sulphobenzyl)-methylamine of the formula:—



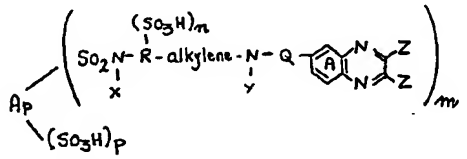
and 3.5 ml. concentrated hydrochloric acid are introduced and the reaction carried out in the presence of pyridine. After the pyridine has been distilled off, subsequent acylation is carried out by means of 2,3-dichloroquinoxaline-6-carboxylic acid chloride, as described in Example 1.

The dyestuff obtained corresponds, in its free acid state, to the formula:—



WHAT WE CLAIM IS:—

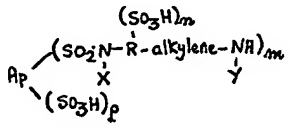
1. Dyestuffs of the general formula:—



wherein Ap means the radical of a metal-containing phthalocyanine dyestuff, R represents an aromatic carbocyclic radical, X and Y, which may be the same or different, denote hydrogen atoms or unsubstituted or substituted alkyl, aralkyl or cycloalkyl radicals, "alkylene" denotes an alkylene radical containing 1—4 carbon atoms, one Z means a halogen atom, the other Z stands for a halogen atom or the residue of a hydroxy compound linked to the heterocyclic ring *via* the —O— atom, Q stands for —OC— or —O_2S—, *n* is 0, 1 or 2, *m* an integer of from 1—4 and *p* is an integer of from 1—8, the sum of *p* and *m* being less than 9; and wherein the ring A may contain further substituents.

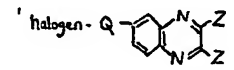
2. Phthalocyanine dyestuffs according to claim 1, which are hereinbefore specifically exemplified.

3. Process for the production of phthalocyanine dyestuffs according to claim 1, wherein, in a phthalocyanine dyestuff of the general formula:—



in which Ap, R, X, Y, "alkylene", *m*, *n* and *p* have the same meaning as above, the

terminal group —NH is condensed with a compound of the general formula:—



wherein "halogen" stands for a halogen atom and Q and Z have the same meanings as above.

4. Process according to claim 3, wherein the amino-phthalocyanine dyestuff is condensed with 2,3-dichloroquinoxaline-6-carboxylic acid chloride or -6-sulphonic acid chloride.

5. Process for the production of phthalocyanine dyestuffs of the general formula given in claim 1, substantially as hereinbefore described and exemplified.

6. Phthalocyanine dyestuffs according to claim 1, whenever prepared by the process according to any of claims 3 to 5.

7. Cellulose-containing fibre materials, whenever dyed or printed by a phthalocyanine dyestuff according to claim 1.

For the Applicants:
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24, Southampton Buildings, Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.